APPARATUS AND PROCESS FOR THE PREPARATION
OF LOW-IRON SINGLE CRYSTAL SILICON SUBSTANTIALLY
FREE OF AGGLOMERATED INTRINSIC POINT DEFECTS

CROSS-REFERENCE TO RELATED APPLICATIONS

5   This application claims the benefit of U.S.
Provisional Application No. 60/258,296, filed December
26, 2000.

BACKGROUND OF THE INVENTION

       The present invention relates to a process and
10   apparatus for the preparation of single silicon crystals
having a reduced level of metallic contamination. More
specifically, the present invention relates to a process
and apparatus for the preparation of low-iron impurity
single silicon crystals wherein structural components in
15   the crystal growth chamber of a Czochralski crystal
pulling apparatus have a reduced concentration of iron.
       Single crystal silicon which is the starting
material for most processes for the fabrication of
semiconductor electronic components is commonly prepared
20   with the so-called Czochralski process. In this process,
polycrystalline silicon ("polysilicon") is charged into a
crucible, the polysilicon is melted, a seed crystal is
immersed into the molten silicon and a single crystal
silicon ingot is grown by slow extraction to a desired
25   diameter. After formation of a neck is complete, the
diameter of the crystal is enlarged by decreasing the
pulling rate and/or the melt temperature until the
desired or target diameter is reached. The cylindrical

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main body of the crystal which has an approximately
constant diameter is then grown by controlling the pull
rate and the melt temperature while compensating for the
decreasing melt level. Near the end of the growth

5   process but before the crucible is emptied of molten
silicon, the crystal diameter must be reduced gradually
to form an end-cone. Typically, the end-cone is formed
by increasing the crystal pull rate and heat supplied to
the crucible. When the diameter becomes small enough,

10   the crystal is then separated from the melt.

During the crystal growth process, iron is
incorporated in the crystals through the polycrystalline
silicon charge, the quartz crucible, and graphite hot
zone structural components such as the susceptor,

15   heaters, thermal shields, or insulation which control the
heat flow around the crucible and the cooling rate of the
growing crystal. The iron impurities in the
polycrystalline charge and crucible diffuse throughout
the melt and produce iron concentrations which do not

20   vary along the radial direction of the ingot and/or
wafer. In contrast, metallic impurities which evaporate
out of graphite structural components diffuse into the
growing crystal from the periphery. As a result, the
concentration of metallic impurities in general, and iron

25   in particular, increases radially outwardly from the
central axis to the edge of the crystal. In addition to
a radial variation, the concentration of iron within an
ingot varies axially. Typically, the iron concentration
in the main body of an ingot decreases axially from the

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seed end to the tail end. The axially variation in iron
is due in part to the fact that the earlier grown
portions of the ingot are exposed to the evaporated iron
for a longer period of time than later grown portions of
5   the ingot.

Heavy metals strongly influence the electrical
characteristics of silicon devices. The initial
electrical effect is the introduction of energy levels
near the center of the bandgap of silicon. These levels
10   may act as recombination centers thus decreasing the
minority carrier recombination lifetime, a material
parameter which strongly influences electrical
characteristics such as leakage current, switching
behavior, and storage time in metal oxide semiconductor
15   (MOS) memories. Likewise, the role of the intermediate
energy level as a generation center may affect, and thus
distort, the ideal current-voltage characteristics of the
p-n junction. Metallic impurities frequently cause
various types of lattice defects such as metallic
20   precipitates, stacking faults or dislocations that form
in the active region on the surface of silicon
substrates. These defects on the surface have a fatal
influence on device performance and yield. In
particular, it is known that iron and molybdenum reduce
25   minority carrier lifetimes in silicon wafers, and copper
and nickel can lead to oxygen induced stacking faults in
the resulting crystal.

In order to reduce the risk of crystal contamination
with contaminants which can be outgassed by graphite

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parts located around the growing crystal, it is common
for graphite components within the hot zone to be coated
with a protective barrier layer. Typically, the
protective layer is silicon carbide because of its

5   relatively high purity, chemical stability and heat
resistance. *See, e.g.,* D. Gilmore, T. Arahori, M. Ito,
H. Murakami and S. Miki, "The impact of graphite furnace
parts on radial impurity distribution in CZ grown single
crystal silicon," J. Electrochemical Society, Vol. 145,

10   No. 2, (Feb. 1998), pp. 621-628. Silicon carbide
coatings provide a barrier to impurity outgassing by
sealing the graphite surface, thus requiring impurities
to pass through the coating by grain boundary and bulk
diffusion mechanisms.

15   Although graphite substrates coated with a thin
layer of silicon carbide have been used to overcome this
problem to a certain extent, the introduction of "closed"
hot zone configurations and increasingly stringent
specifications for metal content in silicon wafers have

20   rendered the existing graphite substrates coated with
silicon carbide unsatisfactory. Closed hot zone
configurations have been implemented to reduce the
density of agglomerated intrinsic point defects (e.g., D-
defects, Flow Pattern Defects, Gate Oxide Integrity

25   Defects, Crystal Originated Particle Defects, crystal
originated Light Point Defects and interstitial-type
dislocation loops) by controlling, among other things,
the cooling rate of the growing silicon ingot during
critical temperature ranges (e.g., between about the

solidification temperature, i.e., about 1300°C, and about 1050°C). Typically, the cooling rate is controlled, in part, by including structural components such as upper, intermediate and lower heat shields above the melt

5   surface. *See, e.g.,* U.S. Pat. No. 5,942,302. As a comparison, for ingot temperatures from about solidification, about 1300°C, to about a 1000°C, a closed hot zone design typically limits the cooling rate to about 0.8°C/mm to about 1.0°C/mm whereas a conventional

10   open hot zone design cools the ingot at about 1.4°C/mm to about 1.6°C/mm.

In addition to using closed hot zone designs to avoid the formation of agglomerated intrinsic point defects, single crystal silicon ingots are allowed to

15   dwell at a temperature between the temperature of solidification and a temperature of about 1050°C to about 900°C, and preferably of about 1025°C to about 925°C, for a period of (i) at least about 5 hours, preferably at least about 10 hours, and more preferably at least about

20   15 hours for 150 mm nominal diameter silicon crystals, (ii) at least about 5 hours, preferably at least about 10 hours, more preferably at least about 20 hours, still more preferably at least about 25 hours, and most preferably at least about 30 hours for 200 mm nominal

25   diameter silicon crystals, and (iii) at least about 20 hours, preferably at least about 40 hours, more preferably at least about 60 hours, and most preferably at least about 75 hours for silicon crystals having a nominal diameter greater than 200 mm. It is to be noted,

however, that the precise time and temperature to which
the ingot is cooled is at least in part a function of the
concentration of intrinsic point defects, the number of
point defects which must be diffused in order to prevent
5   supersaturation and agglomeration from occurring, and the
rate at which the given intrinsic point defects diffuse
(i.e., the diffusivity of the intrinsic point defects).

Although closed hot zones effectively reduce
agglomerated intrinsic point defects (e.g., single
10   crystal silicon grown in an open hot zone design
typically has about $1*10^3$ to about $1*10^7$ defects/cm^3,
whereas single crystal silicon grown in a closed hot zone
typically has less than about $1*10^3$ defects/cm^3), the
increased amount of structural graphite, the higher
15   temperatures, the closer proximity of structural
components to the growing ingot and melt, and the longer
duration of the pulling process can contribute to the
increased amount of iron diffusing into the grown
crystal. For example, crystals grown in a typical open
20   hot zone usually have an average iron concentration of
about 1.0 part per trillion atomic (ppta) and an edge
iron concentration of about 1.0 to about 1.5 ppta,
whereas crystals grown in a typical closed hot zone
usually have an average iron concentration of about 5 to
25   about 10 ppta and an edge iron concentration as high as
100 ppta.

U.S. Patent Number 5,919,302, along with
PCT/US98/07305, PCT/US/07365, and PCT/US99/14285 provide
further details for growing single crystal silicon which

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is substantially free of agglomerated defects. All
matter disclosed in the foregoing patent and applications
is hereby incorporated herein for all purposes.

    Therefore, a need exists in the semiconductor
5   industry for a method which will further reduce the level
of metallic contaminants entering the silicon crystal
during the growing process due to particulate generated
from structural components within the hot zone of the
crystal pulling apparatus.

10   BRIEF SUMMARY OF THE INVENTION

    Generally, the present invention is directed to a
crystal pulling apparatus for producing a silicon single
crystal grown by the Czochralski process. More
specifically, the apparatus comprises a growth chamber
15   and a structural component disposed within the growth
chamber. The structural component comprises a substrate
and a protective layer covering the surface of the
substrate that is exposed to the atmosphere of the growth
chamber. The substrate comprises graphite and has a
20   concentration of iron no greater than about $1.5*10^{12}$
atoms/cm^3 and the protective layer comprises silicon
carbide and has a concentration of iron no greater than
about $1.0*10^{12}$ atoms/cm^3.

    The present invention is further directed to a
25   process for controlling the contamination of a silicon
single crystal with iron during the growth of the silicon
crystal. The process comprises pulling the silicon
single crystal from a pool of molten silicon within a

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growth chamber of a crystal pulling apparatus constructed
with a structural component comprising a substrate and a
protective layer covering the surface of the substrate
that is exposed to the atmosphere of the growth chamber.
The substrate comprises graphite and has a concentration
of iron no greater than about $1.5*10^{12}$ atoms/cm^3. The
protective layer comprises silicon carbide and has a
concentration of iron no greater than about $1.0*10^{12}$
atoms/cm^3.

Other objects and features of the present invention
will be in part apparent and in part pointed out
hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

Fig. 1 is a diagram of a silicon single crystal
pulling apparatus.

Fig. 2 is a diagram of an apparatus used to diffuse
iron from graphite and silicon carbide coated graphite
samples into a silicon wafer in order to determine the
iron concentration in the samples.

Fig. 3 is a graph which shows the concentrations of
iron in four different graphite samples when uncoated and
coated with two different silicon carbide layers.

Fig. 4 is a graph which shows the average edge iron
concentration as a function of axial position for three
ingots pulled under three conditions, a hot zone
constructed with conventional structural components, the
same hot zone with an extra 50 liters/min argon purge

gas, and a hot zone constructed with low impurity structural components.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been discovered that by pulling a silicon single crystal within a crystal pulling apparatus comprising a growth chamber, a closed hot zone and high purity structural components, the concentration of iron impurities in the grown crystal is significantly reduced.

Referring now to Fig. 1, there is shown a crystal pulling apparatus indicated generally at 2. The apparatus comprises a crystal growth chamber 4 and a crystal chamber 6. Contained within crystal growth chamber 4 is a silica crucible 8 which contains molten polysilicon 26 for growing the silicon single crystal. A pulling wire (not shown) attached to a wire rotation device (not shown) is used to slowly extract the growing crystal during operation. Also contained within the crystal growth chamber 4 are several structural components which surround the crucible such as a susceptor 14 for holding the crucible in place, a melt heater 16 for heating the silicon melt, and a melt heater shield 18 for retaining heat near the crucible. A growth chamber with a closed hot zone design may also contain structural components such as a lower heat shield 31 that comprises an inner reflector 32, an outer reflector 33 and an insulation layer 34 sandwiched between coaxially positioned inner and outer reflectors 32 and 33,

respectively. A closed hot zone design may also comprise
an intermediate heat shield 35, and an upper heater
shield 36. As previously stated, these structural
components are typically constructed of graphite and

5   control the heat flow around the crucible and the rate of
cooling of the silicon single crystal. It should be
recognized by one skilled in the art that other
structural components such as the upper heater 37, upper
insulation support 38, or upper insulation shield 39 may

10   also be prepared for use in accordance with the present
invention.

Fig. 1 also depicts the iron contamination in the
growing single crystal ingot 10 with iron emanating from
structural components within the growth chamber (e.g.,

15   lower heat shield 31, intermediate heat shield 35, and
upper heater shield 36). The portion of ingot 10 which
is shaded 12 (not to scale), represents "edge" iron
contamination of a silicon ingot grown in a closed hot
zone constructed with conventional structural components.

20   Edge iron is the common designation for iron
contamination around the circumference of an ingot/wafer.
Typically the extent of edge iron contamination is
referred to as "edge iron concentration" which is the
average iron concentration for the annular portion of a

25   silicon wafer or main body of an ingot extending radially
inward about 5 millimeters from the circumferential edge.
The extent of edge iron contamination also affects the
"average iron concentration" which is the average

concentration of iron throughout an entire silicon wafer
or main body of an ingot.

In accordance with the present invention, structural
components utilized in a growth chamber comprise a
substrate and a protective layer. The substrate of the
present invention comprises graphite, preferably the
substrate is at least about 99.9% pure graphite, and more
preferably at least about 99.99% or more pure graphite.
Further, the graphite preferably contains less than about
3 ppmw total metals such as iron, molybdenum, copper and
nickel, and more preferably less than about 1.5 ppmw.
The concentration of iron in conventional hot zone
graphite ranges from about $2.8*10^{16}$ atoms/cm^3 (1.0 ppmw)
to about $1.4*10^{15}$ atoms/cm^3 (0.05 ppmw). However, the
concentration of iron in a substrate used in accordance
with the present invention is no more than about $1.5*10^{12}$
atoms/cm^3, preferably no more than about $1.0*10^{12}$
atoms/cm^3, more preferably no more than about $0.5*10^{12}$
atoms/cm^3, and still more preferably no more than about
$0.1*10^{12}$ atoms/cm^3.

The protective layer covering at least the surface
of the substrate which is exposed to the atmosphere of
the growth chamber comprises silicon carbide, preferably
the protective layer comprises between about 99.9% to
about 99.99% silicon carbide. Preferably, the entire
surface of the substrate is covered with the protective
layer. Preferably, the silicon carbide protective
coating contains less than about 2 ppmw total metals such
as iron, molybdenum, copper and nickel, and more

preferably less than about 1.5 ppmw. The concentration
of iron in conventional hot zone silicon carbide coatings
ranges from about 0.8 to about 0.5 ppmw. In contrast,
the concentration of iron in the protective coating used

5   in accordance with the present invention is no more than
about $1.0*10^{12}$ atoms/cm^3, preferably no more than about
$0.5*10^{12}$ atoms/cm^3 of iron, and more preferably no more
than about $0.1*10^{12}$ atoms/cm^3 of iron. The thickness of
the protective coating is generally at least about 75

10   micrometers, preferably between about 75 and about 125
micrometers, and more preferably about 100 micrometers.

According to the process of the present invention,
the average iron concentration and the edge iron
concentration in a single crystal silicon ingot grown in

15   a closed hot zone is reduced by replacing at least one
conventional hot zone component with at least one low-
iron impurity component constructed in view of the
foregoing (e.g., upper heater, upper heater shield
intermediate heat shield, the inner reflector, the outer

20   reflector and the insulation layer of the lower heat
shield, intermediate heat shield, upper insulation
support, and upper insulation shield). More
specifically, the iron concentration (average and edge)
in the single crystal silicon is reduced by using at

25   least one low-iron impurity structural component in a
location in which the component will reach at least about
950°C for at least about 80 hours of the growth process
and is within about 3 cm to about 5 cm from silicon melt
or the ingot. It has been observed that the average and

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edge iron concentrations decrease with increasing numbers
of such low-iron structural components within the growth
chamber. Thus, preferably more than one conventional hot
zone component is replaced with a low-iron component.

5   For example, it has been observed that silicon
ingots/wafers having an edge iron concentration below
about 5 ppta and an average iron concentration below
about 3 ppta are produced by replacing at least the
following six conventional components with low iron

10   impurity components during the ingot growth process: the
upper heater, the upper heater shield, the intermediate
heat shield, and the inner reflector, the outer reflector
and the insulation layer of the lower heat shield.
Preferably, the edge iron concentration is below about 3

15   ppta and the average iron concentration is below about 2
ppta, and more preferably the edge iron concentration is
below about 1 ppta and the average iron concentration is
below about 0.8 ppta. Preferably, two additional
components are replaced: the upper insulation support,

20   and the upper insulation shield. More preferably, all
structural components which reach at least about 950°C
for at least about 80 hours of the growth process and are
within about 3 cm to about 5 cm from the silicon melt or
growing ingot are replaced with low-iron impurity

25   structural components.

Definitions

As used herein, the following phrases or terms shall
have the given meanings: "agglomerated intrinsic point

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defects" mean defects caused (i) by the reaction in which
vacancies agglomerate to produce D-defects, flow pattern
defects, gate oxide integrity defects, crystal originated
particle defects, crystal originated light point defects,

5   and other such vacancy related defects, or (ii) by the
reaction in which self-interstitials agglomerate to
produce dislocation loops and networks, and other such
self-interstitial related defects; "agglomerated
interstitial defects" shall mean agglomerated intrinsic

10   point defects caused by the reaction in which silicon
self-interstitial atoms agglomerate; "agglomerated
vacancy defects" shall mean agglomerated vacancy point
defects caused by the reaction in which crystal lattice
vacancies agglomerate; "substantially free of

15   agglomerated intrinsic point defects" shall mean a
concentration of agglomerated defects which is less than
the detection limit of these defects, which is currently
about 10^3 defects/cm^3; "radius" means the distance
measured from a central axis to a circumferential edge of

20   a wafer or ingot.

        The present invention is further illustrated by the
following examples which are merely for the purpose of
illustration and are not to be regarded as limiting the
scope of the invention or manner in which it may be

25   practiced.

Example 1

Determining an Acceptable Concentration
of Iron Impurity in Closed Hot Zone Structural Components

5   A horizontal furnace tube was used to expose a
monitor wafer via gas diffusion to four samples: 1) a
standard graphite sample without any protective coating;
2) the standard graphite coated with silicon carbide from
supplier A; 3) the standard graphite coated with silicon

10   carbide from supplier B; and 4) the standard graphite
coated with silicon carbide from supplier C. The samples
were coupons about 50mm x 50mm x 25mm in size. A fused
silica mask was utilized to separate the monitor wafer
from each test sample. Four holes in the mask allowed

15   the monitor wafer to be exposed to gases generated from
the sample materials. Referring to Fig. 2, each test
stack consisted of a monitor wafer 50 for measuring the
amount of iron transferred via diffusion, a fused silica
mask 51 on top of the monitor wafer, and a sample 52 on

20   top of a hole 53 in the mask. For each run, one wafer
was used as a background sample and did not have a mask
or samples on it.

           Each of the samples were tested to measure iron
diffusivity to the monitor wafer at three different

25   temperatures: 800°C, 950°C and 1100°C. The samples were
held at atmospheric pressure throughout the two hour heat
treatment, and a stream of argon gas over the wafers was
maintained.

           After each heat treatment, the wafer was sliced into

30   quarter sections; each section containing the iron

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diffused from each sample. The minority carrier lifetime
was determined for each wafer section and the background
wafer. The minority carrier lifetime was used to
determine the amount of iron present in the silicon wafer
5   using the surface photovoltaic technique developed by G.
Zoth and W. Bergholz described in the *Journal of Applied
Physics*, vol. 67, (1990), pp. 6764-6771. The minority
carrier lifetime was measured by injecting carriers into
the silicon wafer sample by means of light and observing
10   their decay by monitoring the change in the surface
photovoltage effect. The surface photovoltage technique
is the most sensitive method of measuring carrier
diffusion length and is an accurate method for the
quantitative evaluation of iron in silicon wafers. The
15   method is based on the fact that, in silicon, iron atoms
react with negatively charged boron acceptor atoms to
form Fe-B pairs. Typically, the Fe-B pairs are generated
by annealing the samples at about 70°C for about 30
minutes. When heated, a portion of the Fe-B pairs
20   disassociate and generate interstitial iron (Fe_i) defects.
All the Fe-B pairs disassociate, however, with
illumination using a 250-Watt tungsten-halogen lamp.
See, e.g., J. Lagowski, P. Edelman, O. Millic, W. Henly,
M. Dexter, J. Jastrezebski and A. M. Hoff, *Applied
25   Physics Letters*, vol. 63, (1993), pp. 3043-3045. The
concentration of iron in silicon is determined by
comparing the minority carrier lifetime values at the two
states set forth in the following equation:

$$[Fe] = (0.7/A) \times (10^{16}) \times (1/L_1^2 - 1/L_0^2) \qquad (1).$$

L_1 and L_0 are minority carrier diffusion lengths in
microns before and after the dissociation of Fe-B pairs,
respectively, and A is the fraction of Fe-B pairs
dissociated during thermal activation.

Table 1

Iron Evolved from a Structural Component
as a Function of Temperature

Temperature Structural Component	800°C (atoms/cc)	950°C (atoms/cc)	1100°C (atoms/cc)
Uncoated Graphite	1.24×10^{12}	1.35×10^{13}	1.51×10^{14}
SiC coated graphite - Supplier A	9.37×10^{11}	3.52×10^{13}	7.45×10^{14}
SiC coated graphite - Supplier B	1.18×10^{11}	9.87×10^{12}	8.98×10^{13}
SiC coated graphite - Supplier C	9.71×10^{12}	9.71×10^{13}	9.37×10^{13}

The results in listed Table 1 indicate that the
amount of iron evolved from a structural component
increases with increasing temperature. At present, the

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maximum temperature that can be reached by this method is
1100°C; during a typical closed hot zone growth process
structural components can reach about 1250°C for about 80
hours. Results to date, however, indicate that most of

5   the iron present in the sample coupons come out in the
form of vapor at 1100°C. Thus, testing a sample at
1100°C in accordance with the foregoing procedures
provides an accurate measurement of the total
concentration of iron impurity within the sample.

10   Using the foregoing procedures, the concentration of
iron in the graphite of four suppliers was determined
without a silicon carbide coating and with two different
coatings. The results of the test, depicted in Fig. 3,
clearly indicate that there is significant variability in

15   the concentration of iron in the graphite from the
suppliers that were tested. Also, the results indicate
that in some cases adding a coating may substantially
increase the amount of iron evolved (*see*, graphite B,
coating X and graphite D, coating X). On the other hand,

20   the coating may decrease the amount of iron evolved (*see*,
graphite A, coating Y; graphite C, coating Y; and
graphite D, coating Y). The results clearly indicate
that the silicon carbide coating designated X has a
higher iron concentration than the Y coating. Thus, in

25   contrast to Gilmore et al. at p. 626, to effectively
control the amount of iron contamination in single
crystal silicon grown in a growth chamber having a closed
hot zone the concentration of iron in the graphite <u>and</u>
the silicon carbide coating must be controlled.

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Example 2

Pulling Single Crystal Silicon in a
Growth Chamber containing Reduced Iron Impurity
Structural Components

5   The concentration of iron impurity in single crystal
silicon ingots grown in a Czochralski crystal puller
having a closed hot zone design constructed with
conventional structural components was compared to that
achieved using low-iron structural components.

10   Specifically, three ingots were pulled under three
conditions, a hot zone constructed with conventional
structural components, the same hot zone with an extra 50
liters/min argon purge gas, and a hot zone constructed
with low impurity structural components. The low iron
impurity structural components used in the growth chamber

15   were the upper heater, the upper heater shield, the
intermediate heat shield, the inner reflector, the outer
reflector and the insulation layer of the lower heat
shield, the upper insulation support, and the upper

20   insulation shield. The concentration of iron in the
carbon substrates was about 0.5×10^{12} atoms/cm^3. The
concentration of iron in the silicon carbide protective
layer was about 0.1×10^{12} atoms/cm^3.

Fig. 4 compares the average edge iron of three

25   crystals produced using standard and high purity hot zone
parts as a function of axial position. Fig. 4 clearly
shows that growing silicon crystal grown in chambers
constructed with low iron impurity hot zone parts

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decreases the edge iron concentration. In fact, the
average edge iron concentration in these crystals was
about 50% lower than that of crystals produced using
conventional hot zone parts.

5   In view of the above, it will be seen that the
several objects of the invention are achieved and other
advantageous results attained. It is intended that all
matter contained in the above description shall be
interpreted as illustrative and not in a limiting sense.